

ORGANOLITHIUM INITIATOR FOR ANIONIC POLYMERIZATION, METHOD FOR
PREPARING THE INITIATOR, AND USE OF THE INITIATOR
FOR PREPARING POLYMERS
[Lithiumorganischer Initiator für die anionische Polymerisation,
Verfahren zur Herstellung des Initiators und Verwendung des
Initiators zur Herstellung von Polymeren]

K. Bronstert, et al.

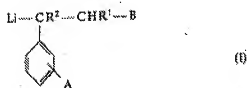
UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. January 2008

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	DE
DOCUMENT NUMBER	(11):	3710468
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	19881013
APPLICATION NUMBER	(21):	P3710468.3
APPLICATION DATE	(22):	19870330
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	C07F 1/02
PRIORITY	(30):	
INVENTOR	(72):	Bronstert, K.; Walter, H.
APPLICANT	(71):	BASF AG
TITLE	(54):	ORGANOLITHIUM INITIATOR FOR ANIONIC POLYMERIZATION, METHOD FOR PREPARING THE INITIATOR, AND USE OF THE INITIATOR FOR PREPARING POLYMERS
FOREIGN TITLE	[54A]:	Lithiumorganischer Initiator für die anionische Polymerisation, Verfahren zur Herstellung des Initiators und Verwendung des Initiators zur Herstellung von Polymeren

1. An organolithium initiator for anionic polymerizations, characterized in that the initiator has a carbon-lithium bond and at least one heteroatom-lithium bond, secondary nitrogen or oxygen being possible heteroatoms.

2. An initiator as recited in Claim 1, characterized by the general formula (I)



where

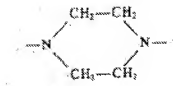
- a) R^1 is an alkyl or aryl radical,
- b) R^2 is an alkyl radical or a hydrogen atom,
- c) A is a $-\text{CH}_2-\text{X}^1-\text{Li}$ radical and B a hydrogen atom,

where X^1 can stand for

- i) $-\text{NR}^3-$, where R^3 is an alkyl or aryl radical or a combination of alkyl and aryl radical and R^3 can optionally contain an additional nitrogen-lithium or oxygen-lithium bond or for
- ii) $-\text{O}-$ or for
- iii) $-\text{Z}^1-\text{R}^4-\text{Z}^2-$, where R^4 is an alkylene or arylene radical or a combination of alkylene and arylene radical, Z^1 is an oxygen atom

* Number in the margin indicates pagination in the foreign text.

or an alkyl or aryl-substituted nitrogen atom, and Z^2 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom,
 iv) or for



or where

A is a hydrogen atom and B a $-\text{CH}_2-\text{X}^2-\text{Li}$ radical,

where X^2 can stand for

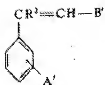
i) $-\text{O}-$ or for

ii) $-\text{NR}^5-$, where R^5 is an alkyl or aryl radical or a combination of alkyl and aryl radical, and

d) the substituent A can be located in an ortho-, meta-, or para-position on the aromatic ring.

3. A method for preparing the initiator as recited in Claim 1, characterized in that an organolithium compound of the general formula R^1-Li is reacted with a ring- or side chain-substituted, vinyl aromatic compound, where R^1 is an alkyl or aryl radical, the substituent of the vinyl aromatic compound has at least one hydrogen atom bonded to a heteroatom, and secondary nitrogen or oxygen atoms are possible heteroatoms.

4. A method as recited in Claim 3, characterized in that the vinyl aromatic compound is of the general formula (II)



(II)

where

a) R^2 is an alkyl radical or a hydrogen atom,

b) A' is a $-\text{CH}_2-\text{X}^1-\text{H}$ radical and B' a hydrogen atom, where X^1 can

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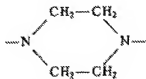
stand for

i) $-\text{NR}^3-$, where R^3 is an alkylene or arylene radical or a combination of alkylene and arylene radical and R^3 can optionally contain an additional nitrogen-lithium or oxygen-lithium bond or for

ii) $-\text{O}-$ or for

iii) $-\text{Z}^1-\text{R}^4-\text{Z}^2-$, where R^4 is an alkylene or arylene radical or a combination of alkylene and arylene radical, Z^1 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom, and Z^2 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom,

iv) or for



or

A' is a hydrogen atom and B' a $-\text{CH}_2-\text{X}^2-\text{H}-$ radical, where X^2 can stand for $-\text{O}-$ or for

i) $-NR^5-$, where R^5 is an alkyl or aryl radical or a combination of alkyl and aryl radical, and

c) the substituent A' can be located in an ortho-, meta-, or para-position on the aromatic ring.

5. Use of an organolithium initiator as recited in Claim 1 for preparing polymers of vinyl aromatic compounds, 1,3-dienes, or mixtures of vinyl aromatic compounds and 1,3-dienes by anionic polymerization.

Description

This invention relates to an organolithium initiator, with whose help it is possible to introduce functional groups at the chain end of polymers. The invention also relates to a method for preparing said organolithium initiators from an organolithium compound and a heteroatom-containing, ring- or side chain-substituted, vinyl aromatic compound, and the use of said organolithium initiators for producing polymers of vinyl aromatic compounds and/or 1,3-dienes.

The use of simple organolithium initiators, such as lithium alkyls, for anionic polymerization of vinyl aromatic compounds and/or dienes has long been known [c.f. K. Ziegler, *Angew. Chem.* 49, 499 (1936); D. J. Worsfold, S. Bywater, *Can. J. Chem.* 38, 1891 (1960)].

Also widely described are end-group functional polymers, where the introduction of functional groups can occur, for example, by using functionalized radical initiators such as 4,4'-azobis(4-cyanovaleric acid) [S. F. Reed, *J. Polym. Sci. A-1*, 9, 2029 (1971)] or 4,4'-azobis(4-cyano-n-pentanol) [J. F. Reed, *J. Polym. Sci. A-1*, 9, 21 (1971)] or by chain breakage of anionically initiated polymers with suitable reagents [R. N. Young, R. P. Quirk, L. J. Fetters, *Adv. Polym. Sci.* 56, 1 (1984); D.O.S. 2.208.340].

However, radical polymerizations have the disadvantage of broad molar mass distributions and the preparation of block copolymers by this method is not practically feasible. The functionalization of anionic polymers by chain breakage is also subject to certain

limitations. First of all, there is only a limited selection of reagents a) that are readily available and b) in which the functionalization occurs without secondary reactions and coupling. Secondly, the only polymers obtained have a functionalized chain end, unless bifunctional initiators are used. Of course, numerous examples of this have been described in the literature [e.g., EP-B1-00 01 977; T. Bastelberger, H. Höcker, Makromol. Chem. 125, 53 (1984); F. Bandermann, H. D. Speikamp, L. Weigel, Makromol. Chem. 126, 2017 (1985)], but in practice they always yield more or less high portions of monofunctional by-products.

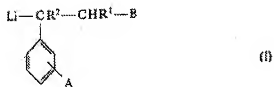
A little traveled path to functionalized polymers using the anionic polymerization technique is the use of functionally substituted initiators. Since the functional groups of interest, i.e., that that are suitable for subsequent reactions at the chain end, would enter into undesired secondary reactions with the carbanionic portion of the initiator molecule, they must be masked. Examples of this are organolithium initiators having primary amino groups that are protected with trimethylsilyl groups [D. N. Schulz, et al., J. Polym. Sci., Polym. Chem. Ed. 15, 2401 (1977)] or initiators with acetalated hydroxyl groups [D. N. Schulz, et al., J. Polym. Sci., Polym. Chem. Ed. 12, 153 (1974)]. However, preparation of these initiators involves a great deal of preparatory work. Another disadvantage of the above-mentioned initiators with masked primary amino groups is their poor solubility in nonpolar solvents.

US Patent 3,439,049 describes p-lithiophenoxide and derivatives thereof as anionic polymerization initiators. However, these compounds are limited to aryl functionalization and preparative methods with low yields.

The object was to produce functionally substituted organolithium initiators and, at the same time, to overcome the above-mentioned disadvantages. This object was achieved with an organolithium /4 initiator in accordance with Claims 1 and 2 and a method of producing such initiators in accordance with Claims 3 and 4.

Subject matter of the invention is therefore an organolithium initiator for the anionic polymerization of vinyl aromatic compounds, 1,3-dienes, or mixtures of vinyl aromatic compounds and 1,3-dienes, whereby the initiator has a carbon-lithium bond and at least one heteroatom-lithium bond and whereby secondary nitrogen and oxygen atoms are possible as heteroatoms.

The initiator preferably is of the general formula:

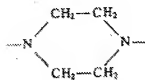


where

- a) R^1 is an alkyl or aryl radical,
- b) R^2 is an alkyl radical or a hydrogen atom,
- c) A is a $-\text{CH}_2-\text{X}^1-\text{Li}$ radical and B a hydrogen atom,

where X^1 can stand for

- i) $-\text{NR}^3-$, where R^3 is an alkyl or aryl radical or a combination of alkyl and aryl radical and R^3 can optionally contain an additional nitrogen-lithium or oxygen-lithium bond or for
- ii) $-\text{O}-$ or for
- iii) $-\text{Z}^1-\text{R}^4-\text{Z}^2-$, where R^4 is an alkylene or arylene radical or a combination of alkylene and arylene radical, Z^1 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom, and Z^2 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom,
- iv) or for



or where

A is a hydrogen atom and B a $-\text{CH}_2-\text{X}^2-\text{Li}$ radical,

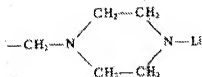
where X^2 can stand for

- i) $-\text{O}-$ or for
- ii) $-\text{NR}^5-$, where R^5 is an alkyl or aryl radical or a combination of alkyl and aryl radical, and

d) the substituent A can be located in an ortho-, meta-, or para-position on the aromatic ring.

Particularly preferable is an initiator in which the radical R^1 is an n-butyl- or s-butyl radical, in which the radical R^2 is a hydrogen atom or a methyl radical, in which the radical R^3 is an n-

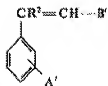
butyl- or tert-butyl radical, and/or in which the substituent A has the structure $-\text{CH}_2-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{O}-\text{Li}$, $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{Li}$, or



An additional subject matter of the invention is a method for preparing the initiator of Claim 1, whereby an organolithium compound of the general formula R^1-Li is reacted with a ring- or side chain-substituted, vinyl aromatic compound, where R^1 is an alkyl or aryl radical, the substituent of the vinyl aromatic compound has at least one hydrogen atom bonded to a heteroatom, and secondary nitrogen or oxygen atoms are possible heteroatoms.

The vinyl aromatic compound is preferably of the general formula

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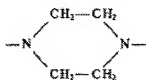
(II)

where

- a) R^2 is an alkyl radical or a hydrogen atom,
- b) A' is a $-\text{CH}_2-\text{X}^1-\text{H}$ radical and B' a hydrogen atom,

where X^1 can stand for

- i) $\text{-NR}^3\text{-}$, where R^3 is an alkyl or aryl radical or a combination of alkyl and aryl radical and R^3 can optionally contain an additional nitrogen-lithium or oxygen-lithium bond or for
- ii) -O- or for
- iii) $\text{-Z}^1\text{-R}^4\text{-Z}^2\text{-}$, where R^4 is an alkylene or arylene radical or a combination of alkylene and arylene radical, Z^1 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom, and Z^2 is an oxygen atom or an alkyl or aryl-substituted nitrogen atom,
- iv) or for



where

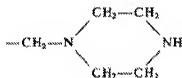
A' is a hydrogen atom and B' a $\text{-CH}_2\text{-X}^2\text{-H}$ radical, where X^2 can stand for $\text{-NR}^5\text{-}$, R^5 being an alkyl or aryl radical or a combination

- i) -O- or for
- ii) $\text{-NR}^5\text{-}$, where R^5 is an alkyl or aryl radical or a combination of alkyl and aryl radical, and

c) the substituent A' can be located in an ortho-, meta-, or para-position on the aromatic ring.

Particularly preferable is a method in which the radical R^1 is an n-butyl- or s-butyl radical, in which the radical R^2 is a hydrogen atom or a methyl radical, in which the radical R^3 is an n-butyl- or

tert-butyl radical, and in which the substituent A' has the structure
 $-\text{CH}_2-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{OH}$, $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$, or



where the reaction of the organolithium compound with the ring- or side chain-substituted vinyl aromatic compound is carried out in such a way that the molar ratio of organolithium compound to vinyl aromatic compound is in the range of $(n+0.5):1$ to $(n+1.5):1$, where n is the number of hydrogen atoms bound to the heteroatoms. The molar ratio of organolithium compound to vinyl aromatic compound is preferably $(n+0.9):1$ to $(n+1.0):1$, where n is the number of hydrogen atoms bound to heteroatoms.

The start of polymerization is triggered by the carbon-lithium bond. Under the chosen conditions, the heteroatom-lithium bond is polymerization inactive and in the polymerization of dienes it has little effect on the microstructure, i.e. on the ratio of 1,2- to 1,4-units. After completion of the polymerization, the functional group (hydroxy or secondary amino group) is released by hydrolysis of the heteroatom-lithium bond, e.g. with water or alcohol. If the polymerization is discontinued with one of the usual functionalization agents, then bifunctional polymers are obtained that can be crosslinked, for example, in further reactions.

Preparation of the inventive initiators is likewise subject matter of this invention. This is accomplished by reacting an organolithium compound of the general formula R^1-Li with a ring- or side chain-substituted vinyl aromatic compound. R^1 is an alkyl or aryl radical, preferably an n- or s-butyl radical. The vinyl aromatic compound has in its ring substituent or side chain substituent at least one hydrogen atom bound to a heteroatom. Oxygen and/or secondary nitrogen atoms are possible heteroatoms. /6

It may be necessary for the substituted vinyl aromatic compound to be prepared in a preliminary step. The commercially available chloromethylstyrene isomer mixture has proven to be a favorable starting material in many cases. For example, it can be reacted in simple condensation reactions with primary amines, with piperazine, with ethanol amine and its derivatives, or with glycol-like compounds to form the desired ring-substituted vinyl aromatic compounds. Another possibility is the hydrolysis of chloromethylstyrenes, described in US Patent 3,069,399. Cinnamyl alcohol may be mentioned as an example of another inexpensive starting compound. These examples serve only to illustrate the vinyl aromatic compounds used to prepare the initiators of this invention, without limiting their number or type, and they may be assumed to be known per se.

The initiators of this invention are prepared in such a way that the molar ratio of organolithium compound to vinyl aromatic compound is in the range of $(n+0.5):1$ to $(n+1.5):1$, where n is the number of

hydrogen atoms bound to the heteroatoms. A molar ratio of $(n+0.9):1$ to $(n+1.0):1$ is preferable.

The preparation occurs under inert conditions, as those that are commonly used in handling organometallic compounds and that are known to those skilled in the art. The work is expediently done in the presence of an inert solvent, where it is unimportant whether the organolithium component is initially present in the solvent and the vinyl aromatic compound is then added or whether the reverse mixing sequence is chosen. The amount of solvent can be varied over a range of 5.00 to 99.9 wt% directly in the polymerization reactor in the desired concentration, without affecting the nature of the initiator immediately before the beginning of polymerization. The reaction is carried out between 0 and +70°C, preferably between +15 and +40°C. Temperatures lower than 0°C are possible, but provide no advantages.

It is an advantage of the inventive initiators that they can be used for preparing polymers of vinyl aromatic compounds, 1,3-dienes, or mixtures of vinyl aromatic compounds and 1,3-dienes by anionic polymerization.

The molar mass of the polymers obtained is 1,000 to 1,000,000, preferably 5,000 to 200,000, the molecular structure of the polymers can correspond to that of a homopolymer or a statistical copolymer, or a block copolymer with sharp or blurred block transition or a combination of the above-mentioned types, bifunctional polymers of vinyl aromatic compounds, 1,3-dienes, or mixtures of vinyl aromatic

compounds and 1,3-dienes can be produced by anionic polymerization using at the same time a functionalized terminating agent, whose molar mass is 500 to 300,000, preferably 1,000 to 100,000 and where the molecular structure of the polymers can correspond to a homopolymer or a statistical copolymer or a block copolymer with sharp or blurred block transition or a combination of the above-mentioned types.

The bifunctional polymers can be used to prepare crosslinked products and the other polymers to produce thermoplastic molding materials. The polymers that are produced are made of vinyl aromatic compounds, preferably butadiene and isoprene. The polymers are prepared under typical anionic polymerization conditions, which are known per se to those skilled in the art.

At the end of the polymerization, it is interrupted wither directly with alcohol or water or it is first reacted with one of the known functionalizing agents and then with alcohol or water. In the former case, the functional groups (hydroxy or secondary amino groups) are released with splitting of the heteroatom-lithium bonds and polymers are obtained with a functionalized chain end. In the latter case, the polymers possess a bifunctional nature with functional groups at both chain ends.

Suitable functionalization agents are, for example, oxirans such as ethylene oxide and propylene oxide, thirans, such as ethylene sulfide and propylene sulfide, 1,5-diaza-[3,1,0]-bicyclohexane,

Schiff bases, chloromethylstyrene, etc. and the incorporated functional groups are, for example, hydroxy, mercapto, amino, vinyl, and other groups. For each mole of lithium (carbon + heteroatom bound) that is used, 1.0 to 1.5 mol functionalization agent is needed. The interruption functionalization occurs in a manner that is known to those skilled in the art [c.f., for example, DE-A 28 13 328, DE-C 35 27 909, German Patent Application P 36 11 421.9].

Many of the bifunctional polymers can be crosslinked. Suitable crosslinking agents are, for example, polyisocyanates and polyepoxides. Products based on this are of interest, for example, in the adhesive industry.

The inventive polymers can also be used to prepare thermoplastic molding materials. For example, thiirane can be used to produce interrupted, SH-terminated polybutadienes for preparing impact-proof polystyrene.

The following examples serve to illustrate the invention, without limiting it. In all the examples, butyllithium was used as a solution in cyclohexane, the abbreviation "BuLi" being used for this solution.

Example 1

Synthesis of vinylbenzyl piperazine (VBP):

300 ml toluene, 300 g anhydrous piperazine (3,85 mol), and 30 g chloromethylstyrene (0.197 mol; ca. 60% m- and 40% p-isomer) were combined under nitrogen in a stirring flask and stirred for 20 hours

at 90°C. After cooling, the result was shaken out three times with 0.1 N NaOH. The combined aqueous phases were shaken out once again with hexane. The combined organic phases were extracted two more times with dilute NaOH, dried with MgSO_4 , and then concentrated in the rotary evaporator under mild conditions (residue: 37.5 g). The raw /7 product obtained in this way was then distilled at about 0.05 torr (b.p.: 100°C, yield: 59.2% of theor.).

(theor.): C 76.85%, H(theor.): 9.36%, N(theor.): 13.79%
(exper.): C 77.2%, H(exper.): 9.1%, N(exper.): 13.7%

Example 2

Synthesis of t-butylaminomethylstyrene (tBAMS):

300 ml freshly distilled tert-butylamine, 300 ml toluene, and 30 g chloromethylstyrene (0.197 mol; ca. 60% m- and 40% p-isomer) were stirred under nitrogen in a 1-liter autoclave for 24 hours at 90°C. After cooling to room temperature, the tert-butylamine-hydrochloride that was formed was filtered off (20.4 g). The solution was shaken out three times, each time with 500 ml water, and the combined aqueous phases were extracted with ca. 200 ml hexane. The combined organic phases were shaken out two more times with water, then dried with MgSO_4 , and then concentrated in the rotary evaporator under mild conditions (residue: 37.5 g). 38.0. The raw product was then distilled at 0.1 torr (b.p. 63-66°C; yield: 89.1% of theor.).

(theor.): C 82.48%, H(theor.): 10.12%, N(theor.): 7.40%
(exper.): C 82.4%, H(exper.): 10.1%, N(exper.): 7.4%

Example 3

Synthesis of n-butylaminomethylstyrene (nBAMS):

600 g n-butylamine (distilled over CaH_2) and 60.0 g freshly distilled chloromethylstyrene (0.394 mol; ca. 60% m- and 40% p-isomer) were stirred for 3 hours at 70°C. After cooling to room temperature, 500 ml hexane was added and the material shaken out two time each with 1 N NaOH and with water. After drying over MgSO_4 , the solvent was first removed in the rotary evaporator and the residue (56.2 g) was then distilled at 0.001 torr with a short-path still (heating surface temperature: 45-50°C, yield: 70.6% of theor.).
(theor.): C 82.54%, H(theor.): 10.05%, N(theor.): 7.41%
(exper.): C 81.9%, H(exper.): 10.2%, N(exper.): 7.7%

Example 4

Synthesis of N-methyl-N-vinylbenzylethanolamine (MVEA):

300 g freshly distilled N-methylethanolamine was placed in a stirring flask under nitrogen and heated to 70°C. 30.0 g chloromethylstyrene (0.197 mol; ca. 60% m- and 40% p-isomer) was added, the temperature rising to 85°C. The clear, strong yellow colored solution was stirred an additional hour at 60 to 70°C and then separated by distillation from most of the excess N-methylethanolamine. 200 ml cyclohexane was added to the remainder. This solution extracted three times with water and the combined aqueous phases extracted again with cyclohexane. After concentration in a rotary evaporator, a residue of 31.5 g remained, which was

distilled at 0.1 torr (b.p.: 93-95°C, yield: 79.7% of theor.).

According to the ^1H -NMR spectrum, the overwhelming portion (>95%) is a benzylamine derivative and a benzyloether derivative is present only as a minor component [$\delta(\text{R-O-CH}_2\text{-O}) = 4.5$ ppm; $\delta(\text{R-N(CH}_3\text{)-CH}_2\text{-O}) = 3.3$ ppm], i.e., the conversion essentially results in MVEA.

(theor.): C 75.39%, H(theor.): 8.90%, N(theor.): 7.33%, O(theor.): 8.38%

(exper.): C 75.3%, H(exper.): 8.8%, N(exper.): 7.4%, O(theor.) 8.5%

Example 5

Preparation of a 0.5 M initiator solution of VBP

and s-butyllithium (I-1):

40 μl styrene was added to 20 ml freshly distilled cyclohexane in a heated 100 ml 2-necked flask that was cooled in a weak nitrogen stream and fully titrated with s-butyllithium at 40°C. A weak, remaining yellow coloring indicates that no more reactive impurities are present. After the addition of 10.1 mg VBP (0.05 mol), 68.7 ml 1.45 N s-butyllithium solution (0.10 mol) was added dropwise at room temperature under stirring and fully titrated cyclohexane added until a volume of 100 ml was reached. The solution had an intense red coloring.

Example 6

Preparation of a 0.5 M initiator solution of nBAMS
and s-butyllithium (I-2):

The preparation was similar to that in example 5. Instead of /8
VBP, 9.45 g nBAMS was used.

Example 7

Preparation of an amino-terminated polystyrene with I-1:

200 ml cyclohexane and 60 ml styrene (0.523 mol) were placed
under a nitrogen atmosphere at 40°C and fully titrated with 0.1 M s-
butyllithium solution. After the addition of 5.44 ml I-1, the
temperature was adjusted to 60°C and the material stirred for 90 min.
The living polymer solution was interrupted with 2 ml methanol. The
polymer was coagulated by stirring the solution into 400 ml methanol,
then it was dissolved in 200 ml toluene and reprecipitated from 400
ml methanol and then dried at 45°C under a vacuum.

yield: 53.7 g; styrene conversion: >98%,
molar mass by GPC (peak value): 24,000 g/mol;
theoretical molar mass by mole ratio styrene/I-1: 20,000 g/mol.
N(exper.): 0.112%, N(theor.): 0,115%.

Example 8

Preparation of an amino-terminated polystyrene with I-1:

This example was carried out as in example 7. Yield: 53.5 g;
styrene conversion: >98%; molar mass by GPC (peak value): 23,500
g/mol; theoretical molar mass by mole ratio styrene/I-2: 20,000
g/mol. N(exper.): 0.058%, N(theor.): 0,060%.

Example 9

Preparation of amino-terminated polybutadienes with an amino functional initiator based on VBP:

Table 9.1

	9a	9b	9c
VBP/g	263	0.81	0.27
VBP/mmol	13.0	4.0	1.3
0.725 N s-BuLi/ml	35.9	11.1	3.7
s-BuLi/mmol	26.0	8.0	2.6
Molmasse(ber)/g/mol	15 000	49 000	150 000

Key:

	9a	9b	9c
VBP/g			
VBP/mmol			
0.725 N s-BuLi/ml			
s-BuLi/mmol			
molar mass (theor.)/g/mol			

1,000 ml anhydrous cyclohexane and VBP were placed under nitrogen in a stirring flask and s-BuLi was then added slowly. After half the amount of BuLi was added, the color of the solution changed from slightly yellow to an intense red. After the addition of 300 ml butadiene (3.61 mol), which had been freshly purified of aluminum alkyl by distillation, was stirred for 3 hours at 60°C. The red coloring of the polymer solution disappeared as the butadiene was added. The solution remained slightly yellow until the end of the polymerization. It was deactivated with 2 ml methanol, stabilized with a sterically hindered phenol (Kerobit TBK, BASF = 2,6-ditert-

butyl-p-cresol), and then precipitated from 2.5 liter methanol by slow dropwise addition of the polymer solution.

Table 9.2

	9a	9b	9c
Ausbeute/g	195	192	194
Molmasse (GPC)/g/mol	17 000	53 000	150 000
N(gel)/%	0,163	0,054	ca. 0,02
N(ber)/%	0,165	0,053	0,019
1,2-Butadien/%	21,4	12,5	9,1/mol

GPC = gel-permeation chromatography

Key:

	9a	9b	9c
yield/g			
molar mass (GPC)/g/mol			
N(exper.)/%			
N(theor.)/%			
1,2-butadiene/%			

Example 10

Polymerization of butadiene with piperidine/s-butyllithium:

300 ml fully titrated cyclohexane, 1.10 g piperidine (13 mmol) and 9.0 ml 1.45 N s-BuLi (13 mmol) were stirred under a nitrogen atmosphere for 10 minutes at room temperature and then mixed with 100 ml butadiene (1.2 mol). The solution was stirred for 6 hours and then deactivated with methanol. 6.3 g polymer (<10% of theor.) was isolated by precipitation from methanol.

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Example 11

Preparation of an amino-terminated polybutadiene with an amino functional initiator based on nBAMS and 1,5-diaza-[3,1,0]-bicyclohexane as termination reagent:

1,000 ml cyclohexane and 2.5 g nBAMS (13.2 mol) were placed in a stirring flask under nitrogen. 36.4 ml 0.725 n s-BuLi (26.4 mmol) and then 300 ml butadiene (3.61 mol) were slowly added. The solution was stirred for 3.5 hours at 60°C and then cooled to 40°C. A sample A of the reaction mixture was precipitated out of methanol.

A solution of 3.3 g 1,5-diaza-[3,1,0]-bicyclohexane (39.6 mmol) in 4.5 ml cyclohexane was slowly added dropwise to the main quantity. The viscosity increased sharply in the process. After stirring for a half hour at 40°C, a sample B was precipitated out of methanol, 1.198 g hydrazine hydrate (39.6 mmol) in 45 ml ethanol was added to the main quantity, and the result was stirred an additional 20 min. When the hydrazine hydrate was added, the polymer solution immediately became low in viscosity once again. Finally, it was stabilized with Kerobit TBK and then precipitated from 2.5 liter methanol. For analytical purposes, 10 g product and the two intermediate samples A and B were reprecipitated two more times from cyclohexane/ methanol.

N(exp. A): 0.097%, N(theor. A): 0.094%

N(exp. B): 0.45%, N(theor. B): 0.47%

Viscosity number (as in DIN 53 726): 35.7 ml/g

1,2-butadiene: 12.2%

Example 12

Preparation of an amino-terminated polybutadiene with an amino functional initiator based on nBAMS:

The charge was made exactly as in example 10, but after the end of the polymerization it was completely interrupted with 2 ml methanol and further processed.

N(exper.): 0.093%, N(theor.): 0,094%
Viscosity number (as in DIN 53 726): 34.9 ml/g
1,2-butadiene: 12,1%

Example 13

Preparation of an amino-terminated polybutadiene with 1,5-diaza[3,1,0]-bicyclohexane as termination reagent:

1,000 ml fully titrated cyclohexane and 18.2 ml 0.725 N s-BuLi (13.2 m mol) were placed under nitrogen in a stirring flask. 300 ml butadiene (3.61 mol) was added and polymerized to completion, the temperature rising in the process from room temperature to 60°C. After cooling to 40°C, 1.65 g 1,5-diaza[3,1,0]-bicyclohexane (19.8 mmol) in 3 ml cyclohexane was added, the result then being stirred a half hour at constant viscosity at 40°C and finally a sample was taken.

0.99 g hydrazine hydrate (19.8 mmol) in 23 ml ethanol was added to the main quantity and stirred an additional 20 min, before being stabilized with Kerobit TBK and precipitated from 2.5 liter methanol.

10 g product and the intermediate sample were reprecipitated two more times from cyclohexane/methanol.

N(exp. sample): 0.21%, N(theor.): 0.19%

Viscosity number (as in DIN 53 726): 35.0 ml/g

1,2-butadiene: 8.9%

Example 14

Crosslinking amino-terminated polybutadienes with hexamethylene diisocyanate (HMDI):

5 g polymer from each of the examples 11, 12, and 13 was dissolved in 30 ml cyclohexane and then mixed with HMDI under a nitrogen atmosphere. The quantity of HMDI was calculated such that a half mole HMDI was used per mole polymer-bound nitrogen atoms. The solutions were cured for three days in a drying oven at 50°C under a light stream of nitrogen. The soluble portions of the crosslinked material were then determined by extraction with two-times 50 ml cyclohexane (in each case, two days at room temperature in a shaking device) and the surface tackiness of the films was assessed qualitatively.

Table 14

	Example 11	Example 12	Example 13
Soluble portions/%	8	100	100
Tackiness of the film	slight	no film formation	no film formation

Example 15

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Preparation of a mercapto-terminated polybutadiene with an amino functional initiator based on nBAMS and methylthiirane (propylene sulfide, PS) as termination reagent:

1,500 ml fully titrated cyclohexane and 0.44 g nBAMS (2.33 mmol) were placed in a stirring flask at 40°C under a nitrogen atmosphere and 23.3 ml 0.2 N s-BuLi (4.67 mmol) added dropwise. 230 ml butadiene (2.77 mol) was then added, the material was polymerized to completion in 2.5 hours at 30 to 65°C, and a small sample A was taken.

0.36 g polystyrene (PS) (4.87 mmol) was added to the main quantity at 40°C, the result stirred for an hour, and a sample taken. The viscosity of the reaction mixture was very high. 0.3 g glacial acetic acid was used for deactivation. After this, the solution again had a low viscosity. It was stabilized with 0.5% Kerobit TBK (with reference to the polymer) and the product precipitated by slowly stirring it into 4 liters of methanol. 10 g product and the intermediate samples were reprecipitated two more times from cyclohexane/methanol.

N(exp. A): 0.0254% S(exp. B): 0,087%

Viscosity number A (as in DIN 53 726): 93.2 ml/g

1,2-butadiene: 10.1%

Example 16

Preparation of a hydroxyl-terminated polybutadiene with an initiator
based on MVEA:

300 ml fully titrated cyclohexane and 2.48 g MVEA as in example 4 (13.0 mmol) were placed under a nitrogen atmosphere at room temperature in a stirring flask and 35.9 ml 0.725 N s-BuLi (26 mmol) was added in two portions. The reaction mixture was then clouded by a small quantity of a red precipitate.

The temperature was increased to 50°C and 100 ml butadiene (1.2 mol) added dropwise within a period of an hour. A sharp rise in viscosity was observed, which was reversed immediately when interrupted with methanol. At the end of the polymerization, the solution was again completely clear. The polymer was purified and isolated by two-time reprecipitation. Yield: 60 g (92% of theor.); N(exper.): 0.2%, O(exper.): 0.2%

Example 17

Preparation of a hydroxyl-terminated polybutadiene with an initiator
based on cinnamyl alcohol:

300 ml fully titrated cyclohexane and 1.74 g cinnamyl alcohol (13 mmol) were mixed in a stirring flask at 50°C under a nitrogen atmosphere and 35.9 ml 0.725 N s-BuLi (26 mmol) added. The material was then stirred for 2 hours at 50°C and then butadiene (100 ml, 1.2

mol) was added dropwise over a period of an hour. After an additional four hours, the material was cooled to room temperature and stirred for 15 more hours before being deactivated with alcohol. During the polymerization, the viscosity of the solution rose sharply, returning to its initial state upon interruption. The material was processed by two-time reprecipitation from cyclohexane/methanol. Yield: 62 g (95% of theor.); O(exper.): 0.2%

Example 18

Butadiene polymerization with 3-phenylbutanol/s-BuLi:

14 ml 1.45 N s-BuLi (20 mmol) was added to 500 ml fully titrated cyclohexane and 3.0 g 3-phenylbutanol (20 mmol) under a nitrogen atmosphere at room temperature, whereupon a slight heat effect was observed. 150 ml butadiene (1.8 mol) was then added and the reaction mixture stirred for 8 hours at about 30°C. This was then interrupted with 2 ml methanol and the solvent evaporated. A polymeric residue of 2.8 g (ca. 3% of theor.) remained.

Example 18

Preparation of a butadiene-styrene block copolymer with an amino functional initiator based on nBAMS and 1,5-diaza-[3,1,0]-bicyclohexane as termination reagent:

1.6 liter fully titrated cyclohexane and 2.5 g nBAMS (13 mmol) were mixed under nitrogen at room temperature and 35.9 ml 0.725 N s-BuLi (26 mmol) was added. After a half hour, 100 ml butadiene was

added dropwise and after an additional two hours a sample A was taken at 45 to 65°C.

300 ml styrene (2.63 mol) was added to the main quantity at 60°C over the course of 20 min. After a secondary reaction time of 30 min, a sample B was taken. Subsequently, the main quantity was treated as follows: cooling to 40°C, addition of 2.50 g 1,5-diaza-[3,1,0]-bicyclohexane (33.8 mmol, dissolved in 47.5 ml cyclohexane), 30 min secondary reaction, sample C, interruption with 1.70 g hydrazine hydrate (33.8 mmol in 50 ml ethanol). The main quantity and sample were first precipitated from methanol, to which about 0.5% Kerobit TBK, with reference to the polymer, had been added, then twice from toluene/methanol, and finally dried under a vacuum at 40°C.

Sample A:	molar mass (GPC peak value): 10,000 g/mol
Sample B:	molar mass (GPC peak value): 50,000 g/mol
	OsO ₄ decomposition: block polystyrene: 80.2%,
	molar mass (GPC peak value): 38,000 g/mol
Sample C:	N(exper.): 0.15%

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